AIP Applied Physics Letters

Negative magnetoresistance of γ- Fe 2 O 3 observed in γ- Fe 2 O 3 /Ag granular nanocomposites

Jinke Tang, Li Feng, and Joan A. Wiemann

Citation: Applied Physics Letters **74**, 2522 (1999); doi: 10.1063/1.123899
View online: http://dx.doi.org/10.1063/1.123899
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/74/17?ver=pdfcov
Published by the AIP Publishing

Negative magnetoresistance of γ-Fe_2O_3 observed in γ-Fe_2O_3/Ag granular nanocomposites

Jinke Tang,[a] Li Feng, and Joan A. Wiemann
Department of Physics and Advanced Materials Research Institute, University of New Orleans, New Orleans, Louisiana 70148

(Received 15 December 1998; accepted for publication 4 March 1999)

The magnetoresistance of $(\gamma\text{-}Fe_2O_3)_xAg_{100-x}$ (x=50–90), a granular system where insulating magnetic nanoparticles and nonmagnetic metal are intimately mixed, has been studied at room temperature. For high silver concentration ($x\leqslant 70$), samples are metallic and exhibit ordinary positive magnetoresistance. Below the percolation threshold, which is 11.4 vol % of silver (x=71), samples are insulators. Our data suggest that direct tunneling between silver grains across γ-Fe_2O_3 barriers dominates at low temperature and variable range hopping becomes the main transport mechanism at high temperature. The variable range hopping within γ-Fe_2O_3 is believed to be associated with the presence of Fe^{2+} impurities which is determined by Mössbauer spectroscopy. Negative magnetoresistance up to −2% is found in $(\gamma\text{-}Fe_2O_3)_xAg_{100-x}$ ($x\geqslant 72$) in an applied field of 10 kOe at room temperature. It is proposed that the observed negative magnetoresistance is due to the field-dependent hopping rate of electrons from Fe^{2+} to Fe^{3+} which is enhanced due to the alignment of their moments by an applied magnetic field. [S0003-6951(99)03217-9]

Large magnetoresistance has been observed in metal–insulator–metal trilayers, where two magnetic layers are spaced by a thin insulator film.[1,2] The results support the claim that large magnetoresistance is due to the spin polarized tunneling of electrons between two magnetic metals through a thin Al_2O_3 insulator. These findings have attracted much attention because of the interesting problem of ''spin tunneling'' involved in such systems and because of the potential applications of the tunneling devices. The essential features of the observed tunneling magnetoresistance can be explained with the models by Julliere[3] and Slonczewski[4] although further studies of tunneling phenomena in heterogeneous systems are still needed.[5]

On the other hand, the magnetoresistance of half-metallic magnetite Fe_3O_4 has recently been reported.[6] The negative magnetoresistance is associated with intergranular transport of spin-polarized electrons. The negative magnetoresistance has also been attributed to the magnetic field effects on the hopping conductance.[7,8] It is of interest to know the magnetoresistance of maghemite, γ-Fe_2O_3, another common form of iron oxide. Like Fe_3O_4, γ-Fe_2O_3 is ferrimagnetic. However due to the lack of Fe^{2+}, which provides the hopping mechanism for the conductance in Fe_3O_4, γ-Fe_2O_3 is an insulator. Accurate magnetoresistance data of γ-Fe_2O_3 are thus not available.

We report here the study on the magnetoresistance of $(\gamma\text{-}Fe_2O_3)_xAg_{100-x}$ (x=50–90), a granular system where insulating magnetic nanoparticles and nonmagnetic metal are intimately mixed. When the metal concentration is below its percolation threshold, electron transport is dominated by tunneling and variable range hopping, which involves Fe^{2+} impurities in the γ-Fe_2O_3. A sizable negative magnetoresistance is found at room temperature (RT) which we attribute to the increased electron hopping rate between Fe^{2+} and Fe^{3+} due to the alignment of iron moments by an applied magnetic field.

Samples were prepared by mechanical milling. Commercial γ-Fe_2O_3 and Ag powders with various molar ratios, $(\gamma\text{-}Fe_2O_3)_xAg_{100-x}$ where x=50–90, were sealed in a hardened steel grinding vial. Grinding was conducted in a high energy Spex-8000 mill/mixer under slurry (in water) conditions. In order to prevent the formation of α-Fe_2O_3, the mill/mixer was placed in a freezer which has temperature near 0 °C. Powders were heated to 100 °C for several h to drive the water out after 17–19 h of grinding/mixing. X-ray diffraction patterns of the products are those of the mixture of Ag and γ-Fe_2O_3. The average crystallite size of γ-Fe_2O_3 estimated from the x-ray peak broadening is about 20 nm. Mössbauer spectroscopy shows that about 3.7% of iron in γ-Fe_2O_3 is in Fe^{2+} state as indicated by the presence of B' sextet.[9] Since our tests show that original commercial γ-Fe_2O_3 contains essentially no Fe^{2+}, the Fe^{2+} may be the direct result of prolonged ball milling. It is also possible that γ-Fe_2O_3 reacts with the iron from the ball mill and forms slightly reduced γ-Fe_2O_3. Similar chemical process is found in the preparation of FeO from Fe_2O_3 and a steel mill.[10] Granular films of $(\gamma\text{-}Fe_2O_3)_xAg_{100-x}$ of selected compositions were also prepared by pulsed laser deposition (PLD). Similar magnetotransport properties were observed in both the PLD samples and those prepared by mechanical milling. Our discussion will concentrate on the samples made by the latter technique.

Figure 1 shows the room temperature magnetic hysteresis loop of one of the samples $(\gamma\text{-}Fe_2O_3)_{72}Ag_{28}$, on which most of experiments presented in this letter were conducted. Its coercivity of 80 Oe is smaller than the typical values of commercial γ-Fe_2O_3 particles, which is due to the particle

[a]Author to whom correspondence should be addressed; electronic mail: jtang@uno.edu

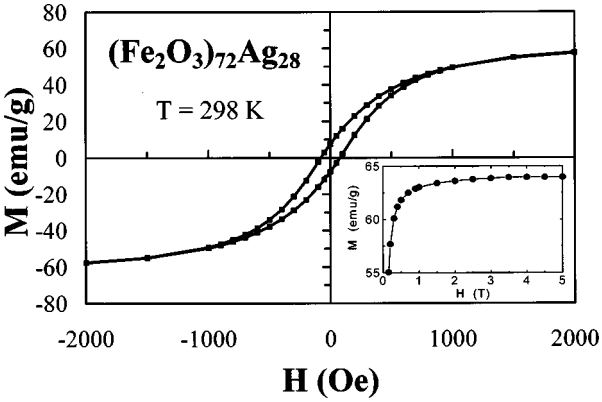

FIG. 1. RT hysteresis loop of $(\gamma\text{-}Fe_2O_3)_{72}Ag_{28}$ between −2000 and 2000 Oe. Inset shows the magnetization as a function of applied field from 0.2 to 5 T.

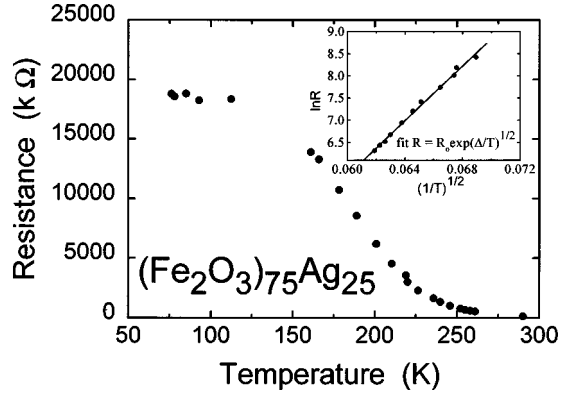

FIG. 3. Resistance as a function of temperature of $(\gamma\text{-}Fe_2O_3)_{75}Ag_{25}$. The inset is the resistance shown in a $\ln R$ vs $(1/T)^{1/2}$ plot together with the fit, $R = R_0 \exp[\Delta/T]^{1/2}$, over temperature range 200–260 K.

size reduction by the mechanical milling. The inset of Fig. 1 shows the magnetization of $(\gamma\text{-}Fe_2O_3)_{72}Ag_{28}$ as a function of applied field from 0 to 5 T. It does not saturate until about 5 T. This will be discussed later in connection with the negative magnetoresistance observed in the system.

Figure 2 shows the resistivity of $(\gamma\text{-}Fe_2O_3)_xAg_{100-x}$. It was measured on a pressed pellet using the four point method. For $x \leqslant 70$, samples exhibit metallic conductivity. For $x \geqslant 72$, samples are insulators. A metal-to-insulator transition is clearly seen at about $x=71$. This corresponds to a volume concentration of 11.4%(Ag) for the percolation limit. The current–voltage (I–V) curves of the samples with $x \leqslant 70$ are straight lines. Their conductivity is determined by the metallic silver. Below its percolation limit, silver no longer forms connected network. The I–V curves show curvature that is consistent with either electron tunneling through barriers or hopping within the barrier.

Resistance as a function of temperature is shown in Fig. 3 for $(\gamma\text{-}Fe_2O_3)_{75}Ag_{25}$. It increases with decreasing temperature initially, then it starts to level off and becomes nearly temperature independent below about 100 K. This is indicative of the tunneling mechanism for the electron transport. The predominate electron transport at low temperatures is most likely the direct tunneling between silver grains across $\gamma\text{-}Fe_2O_3$ barriers.[11] Between 160 K and RT the resistance follows $R = R_0 \exp[\Delta/T]^{1/2}$, which suggests variable range hopping conduction in the presence of a Coulomb gap.[12]

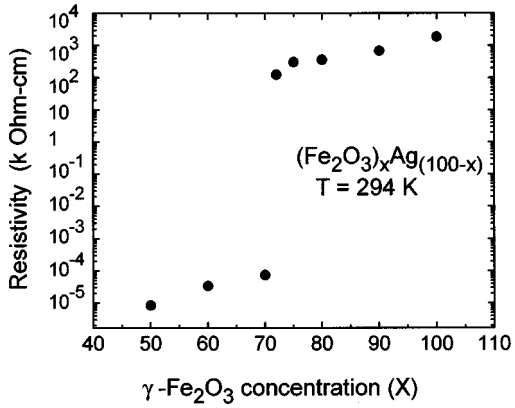

FIG. 2. Resistivity of $(\gamma\text{-}Fe_2O_3)_xAg_{100-x}$, which shows a metallic-to-insulating transition at about $x=71$.

Resistance data are shown in the inset of Fig. 3 in a $\ln R$ versus $(1/T)^{1/2}$ plot together with the fit. The least-squares fit to the experimental data over the shown temperature range (200–260 K) results in a $\Delta = 95\,100$ K. Since there are Fe^{2+} impurities in our samples, their presence should aid the variable range hopping conduction in $\gamma\text{-}Fe_2O_3$.

The magnetoresistance of $(\gamma\text{-}Fe_2O_3)_xAg_{100-x}$ has been studied at RT. For $x \leqslant 70$, magnetoresistance is positive. This is the ordinary magnetoresistance commonly observed in nonmagnetic metals, which originates from the Lorentz force on the electrons in the silver metal. This positive magnetoresistance increases slightly as the silver concentration approaches the percolation limit (Fig. 4). This increase may be related to the much reduced numbers of conduction pathways connected by the silver atoms as the silver concentration decreases. The electrons are forced to take whatever the routes defined by the geometry of the silver network, which may not be necessarily a straight line between the probes.

An abrupt change in the magnetoresistance has been observed for $x \geqslant 72$. Negative magnetoresistance is found for $x=72$, 75, 80, and 90. The resistance of the pure $\gamma\text{-}Fe_2O_3$ is very high and the rather large noise associated with it prevents accurate measurement of its magnetoresistance. The highest magnetoresistance is observed in $(\gamma\text{-}Fe_2O_3)_{72}Ag_{28}$. Its magnetoresistance was measured as a function of applied field in both current parallel to field ($I \| H$) and current perpendicular to field ($I \perp H$) configurations (Fig. 5). Negative magnetoresistance of about ~2% is observed in both configurations around 1 T at room temperature. Figure 5, inset, is the high field magnetoresistance measured up to 5 T,

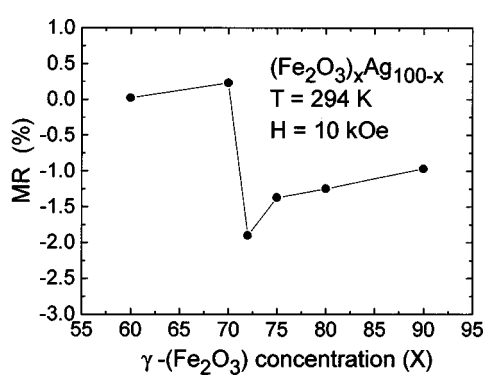

FIG. 4. Magnetoresistance of $(\gamma\text{-}Fe_2O_3)_xAg_{100-x}$.

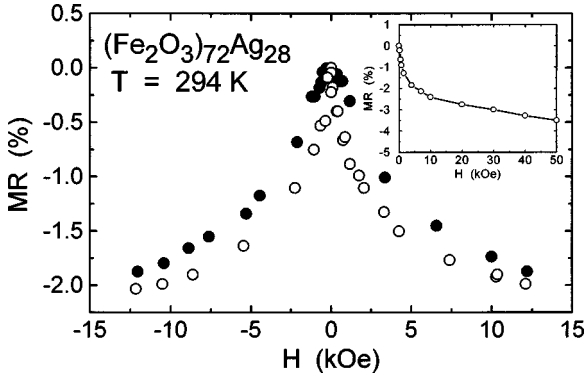

FIG. 5. Magnetoresistance as a function of applied field in both $I \| H$ (open circles) and $I \perp H$ (solid circles) configurations. Inset: high field magnetoresistance measured up to 5 T.

which shows that the change of magnetoresistance starts to slow down as the field reaches about 1 T. The magnetoresistance is -3.5% at 5 T and room temperature. In Fig. 4, the magnitude of the negative magnetoresistance for $x \geqslant 72$ decreases with γ-Fe_2O_3 concentration. The exact reason needs to be further studied. This granular nanocomposite system is also interesting for it allows the tuning of the resistance by an order of magnitude, by changing the γ-Fe_2O_3 concentration from $x=72$ to $x=90$, while maintaining the relative magnetoresistance between 1% and 2%.

We now comment on the possible origin of the negative magnetoresistance in $(\gamma\text{-}Fe_2O_3)_xAg_{100-x}$ $(x \geqslant 72)$. A plausible explanation is the field-dependent electron hopping rate from Fe^{2+} to Fe^{3+}. It is well known that, according to the double exchange theory[13] based on the exchange of electrons between Mn^{3+} and Mn^{4+} ions through the O^{2-} ion in doped perovskite rare earth manganites, the electron hopping probability from Mn^{3+} to Mn^{4+} ions depends on the relative orientation of the two moments and increases as they are aligned in the same direction. We propose that similar mechanism applies to the exchange of electrons between Fe^{2+} and Fe^{3+} in γ-Fe_2O_3. Near RT, the electron transport is predominentely via variable range hopping that involves Fe^{2+} impurities. As the applied field aligns the moments of Fe^{2+} and Fe^{3+} ions in the field direction, the electron hopping rate from Fe^{2+} and Fe^{3+} increases. Comparing the insets of Figs. 1 and 5, there exists a clear correlation between the magnetization and magnetoresistance.

In summary, we have studied magnetoresistance of granular $(\gamma\text{-}Fe_2O_3)_xAg_{100-x}$. Negative magnetoresistance up to -2% has been observed at room temperature in an applied field of 10 kOe when silver concentration is below its percolation threshold, which is 11.4 vol %(Ag) $(x=71)$ for our samples. Tunneling through the insulating γ-Fe_2O_3 is the predominant mechanism of electron transport at low temperature. At high temperature the conduction is mainly via variable range hopping. The observed negative magnetoresistance is believed to arise from the field-dependent electron hopping probability from Fe^{2+} to Fe^{3+} ions which depends on the relative orientations of the magnetic moments of the two ions. Different mechanisms for the observed magnetoresistance, however, cannot be ruled out. Future study may shed more light on the issue.

The authors would like to thank Fred Parker for the Mössbauer data and Ami Berkowitz for very helpful discussions. Research was supported by NSF (DMR-9626297) and DARPA (MDA972-97-1-0003).

[1] J. S. Moodera, L. R. Kinder, T. M. Wong, and R. Meservey, Phys. Rev. Lett. **74**, 3273 (1995).
[2] T. Miyazaki and N. Tezuka, J. Magn. Magn. Mater. **139**, 231 (1995).
[3] M. Julliere, Phys. Lett. **54A**, 225 (1975).
[4] J. C. Slonczewski, Phys. Rev. B **39**, 6995 (1989).
[5] J. M. MacLaren, X. G. Zhang, and W. H. Butler, Phys. Rev. B **56**, 11827 (1997).
[6] J. M. D. Coey, A. E. Berkowitz, L. I. Balcells, F. F. Putris, and F. T. Parker, Appl. Phys. Lett. **72**, 734 (1998).
[7] G. Q. Gong, A. Gupta, G. Xiao, W. Qian, and V. P. Dravid, Phys. Rev. B **56**, 5096 (1997).
[8] S. B. Ogale, K. Ghosh, R. P. Sharma, R. L. Greene, R. Ramesh, and T. Venkatesan, Phys. Rev. B **57**, 7823 (1998).
[9] F. T. Parker and A. E. Berkowitz, Phys. Rev. B **44**, 7437 (1991).
[10] T. Kosmac and T. H. Courtney, J. Mater. Res. **7**, 1519 (1992).
[11] C. Platt, B. Dieny, and A. E. Berkowitz, Appl. Phys. Lett. **69**, 2291 (1996).
[12] B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors* (Springer, Berlin, 1984).
[13] C. Zener, Phys. Rev. **82**, 403 (1951).